Photocyclization Reactions. Part 5 [1].
Synthesis of Dihydrobenzofuranols Using Photocyclization of 2-Alkoxybenzophenones and Ethyl 2-Benzoylphenoxyacetates

Essam Mohamed Sharshira, Satoru Shimada, Mutsuo Okamura,
Eietsu Hasegawa and Takaaki Horaguchi*

Department of Chemistry, Faculty of Science, Niigata Univeristy,
Ikarashi, Niigata 950-21, Japan

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Photocyclization reactions were carried out on 2-alkoxybenzophenones **1a-h** and ethyl 2-benzoylphenoxyacetates **2a-e** in acetonitrile. Irradiation of **1a-h** gave dihydrobenzofuranols **4a-h** in 68-84% yields. Similarly, irradiation of **2a-e** afforded dihydrobenzofuranols **8a-e** in 72-75% yields. Ethyl acrylates **9b-c** were also produced in 6-8% yields from photoreactions of **2b-c**. Substituent effects on cyclization of 1,5-biradical intermediates and reaction pathways are discussed. Benzophenones are useful compounds to prepare dihydrobenzofuranols by photocyclization.

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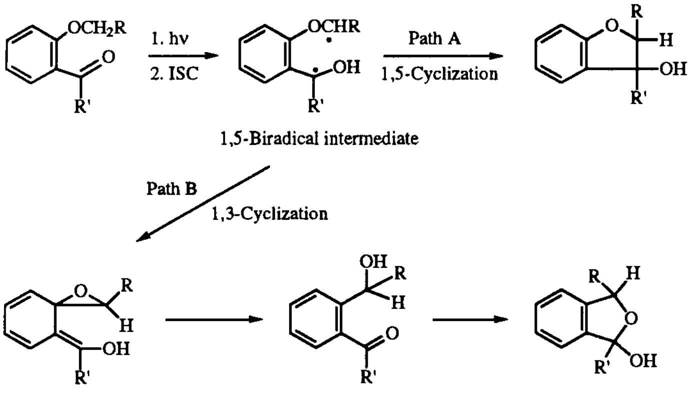
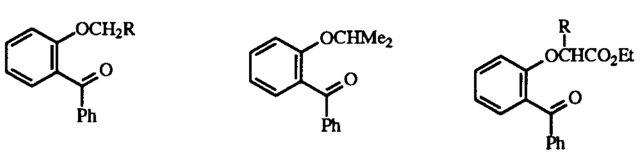
Introduction.

Photocyclization reactions of *o*-substituted aromatic carbonyl compounds have been used for synthesis of benzofuran derivatives. The carbonyl compounds consist of benzaldehydes [2], acetophenones [2b-c,3], benzophenones [3a,3c-d,4], cyclic ketones [1,5], α-dicarbonyl compounds [6] or benzoquinones [7]. In general, photocyclization reactions of carbonyl compounds are considered to proceed via 1, 5-biradical intermediates formed through δ-hydrogen abstraction by carbonyl group as shown in Scheme 1 [3a, 3c, 4a-c, 4e].

Scheme 1



The 1,5-biradicals can undergo 1,5-cyclization to dihydrobenzofuranols (path A) or 1,3-cyclization to spiroenols (path B) [3a, 3c] which rearrange to the corresponding 2-acyl alcohols or their hemiacetals. Preference for path A or path B depends on the kinds of substituents R and R'. For example, when benzophenones (R' = Ph) are used as starting materials, 1,5-cyclization occurs to give dihydrobenzofuranols [3a, 3c]. However, when benzaldehydes (R' = H) and acetophenones (R' = Me) are employed, 1,3-cyclization competes with 1,5-cyclization to afford rearranged products [2b]. Changing R from alkyl group to electron-withdrawing ethoxycarbonyl or cyano group, 1,5-cyclization occurs predominantly even in the photocyclization of acetophenone derivatives [2b]. Though mechanistic studies on photocyclization reactions of benzophenones have been well done [3a,3c, 4a-c,4e], there are a few reports on systematic synthetic studies for dihydrobenzofuranols by photocyclization of benzophenone derivatives [3c,4f]. In this paper, we report synthesis of dihydrobenzofuranols using photocyclization of 2-alkoxybenzophenones **1a-h** (ether compounds of benzophenones) and ethyl 2-benzoylphenoxyacetates **2a-e** (ester compounds of benzophenones) and substituent effects on cyclization of 1,5-biradical intermediates.



1 **1h** **2**

1a, R = H
1b, R = Me
1c, R = Et
1d, R = *i*-Pr
1e, R = Ph
1f, R = CH=CH$_2$
1g, R = CN

2a, R = H
2b, R = Me
2c, R = Et
2d, R = *i*-Pr
2e, R = Ph

Figure 1

Results and Discussion.

2-Alkoxybenzophenones **1a-h** for photocyclization were synthesized in good yields by the reactions of 2-hydroxybenzophenone **3** with methyl iodide, ethyl iodide, propyl iodide, isobutyl bromide, benzyl chloride, allyl bromide, bromoacetonitrile or isopropyl iodide in the presence of tripotassium phosphate as a base. The results are summarized in Scheme 2 and Table 1. Similarly, reactions of 2-hydroxybenzophenone **3** with ethyl bromoacetate, ethyl 2-bromopropionate, ethyl 2-bromobutyrate, ethyl 2-bromo-3-methylbutyrate or ethyl 2-bromo-2-phenylacetate gave the corresponding ester **2a-e**. The results are shown in Scheme 3 and Table 2.

Scheme 2

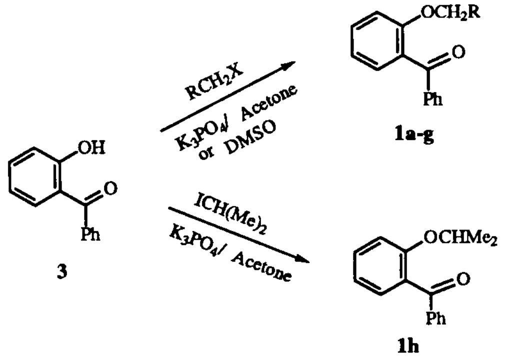
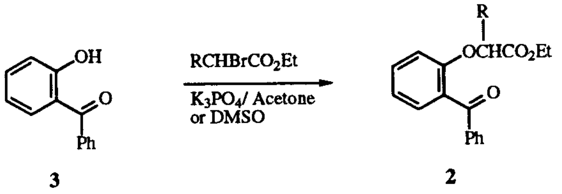


Table 1

Synthesis of 2-Alkoxybenzophenones **1a-h**

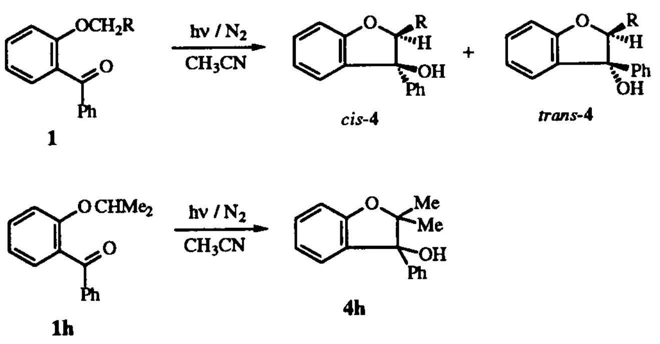
Starting material	Reagent	Base	Solvent	Temperature (°C)	Time (minutes)	R	Product (%)	Yield
3	MeI	K_3PO_4	Acetone	Reflux	180	H	**1a**	85
3	EtI	K_3PO_4	Acetone	Reflux	180	Me	**1b**	92
3	PrI	K_3PO_4	Acetone	Reflux	180	Et	**1c**	89
3	*i*-BuBr	K_3PO_4	DMSO	60	180	*i*-Pr	**1d**	94
3	$PhCH_2Cl$	K_3PO_4	DMSO	60	180	Ph	**1e**	80
3	$BrCH_2CH{=}CH_2$	K_3PO_4	Acetone	Reflux	180	$CH{=}CH_2$	**1f**	98
3	$BrCH_2CN$	K_3PO_4	DMSO	60	180	CN	**1g**	92
3	*i*-PrI	K_3PO_4	Acetone	Reflux	180	-	**1h**	95

Scheme 3



Initially, photocyclization reactions on ether compounds of benzophenones **1a-h** were carried out with 400-W high-pressure mercury lamp (Pyrex filter) in acetonitrile. The results are summarized in Scheme 4 and Table 3.

Scheme 4



When 2-methoxybenzophenone **1a** (R = H) was irradiated, 3-phenyl-2,3-dihydro-3-benzofuranol **4a** was obtained in 68% yield. The yield of **4a** is much better than those (27% and 37%) from 2-methoxybenzaldehyde and 2'-methoxyacetophenone [2b]. The results show that phenyl group of benzophenones favors 1,5-cyclization of 1,5-biradical intermediate to give good yield of dihydrobenzofuranol [3a]. 1,3-Cyclization may occur but rearranged products were not isolated. Similarly, irradiation of 2-isopropoxybenzohenone **1h** gave dihydrobenzofuranol **4h** in 69% yield.

Irradiation of 2-ethoxybenzophenone **1b** (R = Me) produced a mixture of *cis* and *trans* isomers (81%, *cis* and *trans* ratio is 2.4:1) with regard to R and hydroxyl group of 2-methyl-3-phenyl-2,3-dihydro-3-benzofuranol **4b**. Stereoselectivity of *cis* and *trans* isomers was not good in acetonitrile solution. Stereochemistry of *cis* and *trans* isomers on **4b** was determined by considering an anisotropic

Table 2

Synthesis of Ethyl 2-Benzoylphenoxyacetates **2a-e**

Starting material	Reagent	Base	Solvent	Temperature	Time (°C)	R (minutes)	Product	Yield (%)
3	CH_2BrCO_2Et	K_3PO_4	Acetone	Reflux	60	H	**2a**	87
3	$MeCHBrCO_2Et$	K_3PO_4	Acetone	Reflux	60	Me	**2b**	83
3	$EtCHBrCO_2Et$	K_3PO_4	Acetone	Reflux	60	Et	**2c**	90
3	*i*-$PrCHBrCO_2Et$	K_3PO_4	DMSO	70	180	*i*-Pr	**2d**	82
3	$PhCHBrCO_2Et$	K_3PO_4	Acetone	Reflux	60	Ph	**2e**	52

Table 3

Photocyclization Reactions of 2-Alkoxybenzophenones **1a-h**

Starting material	R	Irradiation time (minutes)	Conversion (%)	Product	Yield(%) [a] (*cis*:*trans*) [b]
1a	H	40	100	**4a**	68
1b	Me	20	100	**4b**	81(2.4:1)
1c	Et	30	100	**4c**	77(3.5:1)
1d	*i*-Pr	30	100	**4d**	71(2.6:1)
1e	Ph	25	100	**4e**	81(1.7:1)
1f	$CH=CH_2$	20	100	**4f**	70(1.3:1)
1g	CN	60	100	**4g**	84(1:1.6)
1h [c]	-	30	100	**4h**	69

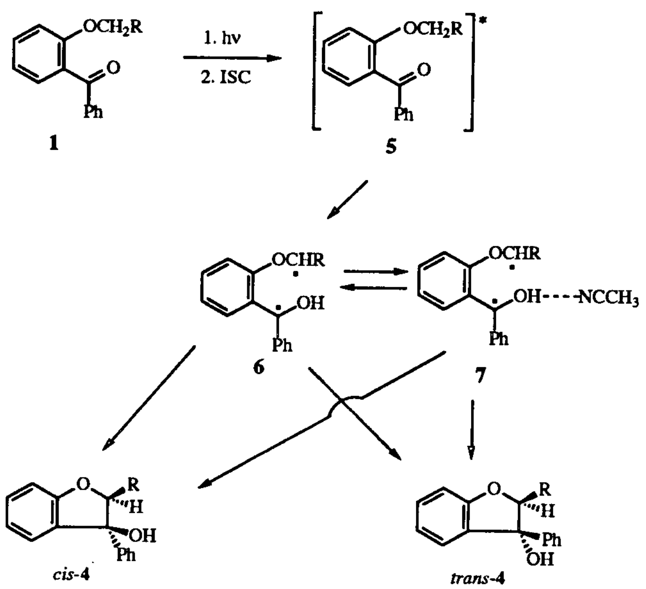
[a] Isolated yield. [b] *Cis* and *trans* isomers with regard to alkyl and hydroxyl groups. [c] 2-Isopropoxybenzophenone.

effect of C_3-phenyl group for C_2-R or C_2-H in the ^1H nmr spectra [3c, 6a]. Generally, in dihydrobenzofuranols C_3-phenyl group shields C_2-R or C_2-H at the *cis* position, that is, C_2-R or C_2-H chemical shift appears at a higher magnetic field than that of *trans* position. When compounds **1c-g** (R = Et, *i*-Pr, Ph, $CH=CH_2$, CN) were irradiated, a mixture of *cis* and *trans* dihydrobenzofuranols **4c-g** were obtained in each case. The *cis*:*trans* ratio ranges from 3.5:1 to 1:1.6, showing low stereoselectivity.

The reaction pathways of photocyclization on **1** are shown in Scheme 5. Irradiation of **1** produces (n, π^*) excited triplet state **5** after intersystem crossing process (ISC). The carbonyl group of **5** abstracts δ-hydrogen to give 1,5-biradicals **6** [3a, 4e] which cyclize directly or after solvation of hydroxyl group to dihydrobenzofuranols **4**. *Cis* and *trans* isomer ratio of dihydrobenzofuranols would be controlled by the steric effect (bulkiness) of R, Ph and OH in the cyclization step of 1,5-biradicals. That is, larger two substituents are arranged apart each other in the cyclization step. If 1,5-biradicals **6** cyclize directly, *cis* isomer would be produced preferentially. However, in acetonitrile, most part of hydroxyl group in 1,5-biradicals would be solvated by acetonitrile using intermolecular hydrogen bonding like **7**. Therefore, the hydroxyl group becomes bulkier than free hydroxyl group. The solvated 1,5-biradicals would give a mixture of *cis* and *trans* isomers of **4**. The hydrogen bonding lowered stereoselectivity of *cis* and *trans* isomers [3a,3c]. In fact, Wagner *et al.* reported that photocyclization of benzophenone derivatives in less polar benzene solution showed high selectivity of *cis* isomer [3c]. Detailed solvent effects in the cyclization step of 1,5-biradicals are under study. Better yields of dihydrobenzofuranols from benzophenones are attributed to fast coupling of 1, 5-biradicals by rotation of benzylic p-orbital around single bond between *o*-alkoxyphenyl ring and benzylic carbon which control 1,3-cyclization of 1,5-biradicals [3a,3c].

Next, photocyclization reactions of ethyl 2-benzoylphenoxyacetates **2a-e** were examined. The results are summarized in Scheme 6 and Table 4.

Scheme 5



Scheme 6

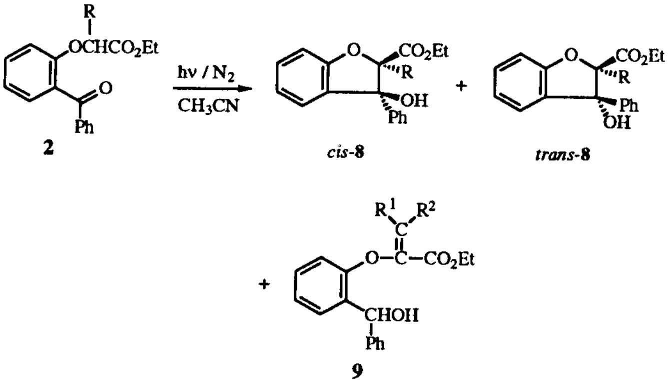


Table 4

Photocyclization Reactions of Ethyl 2-Benzoylphenoxyacetates **2a-e**.

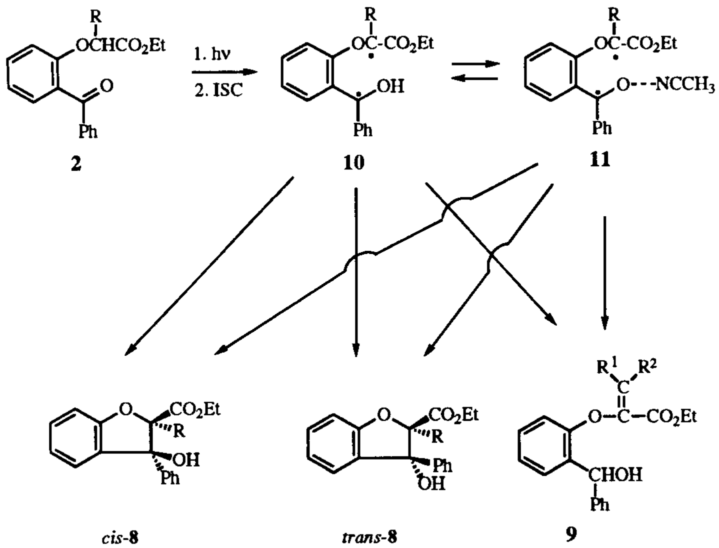
Starting material	R	Irradiation time (minutes)	Conversion (%)	Product **8** (*cis*:*trans*) [a]	Yield(%) [a] **9**[a]
2a	H	30	100	75(1.5:1)	-
2b	Me	15	100	72(4.1:1)	6
2c	Et	20	100	74(5.2:1)	8[c]
2d	*i*-Pr	20	100	75(5.8:1)	0
2e	Ph	25	100	75(17.8:1)	-

[a] *Cis* and *trans* isomers with regard to the ethoxycarbonyl and hydroxyl groups. [b] **9b**, $R^1 = R^2 = H$; **9c**, $R^1 = H$, $R^2 = CH_3$ or $R^1 = CH_3$, $R^2 = H$. [c] *E* and *Z* isomer ratio = 1:4.

Irradiation of ethyl 2-benzoylphenoxyacetate **2a** (R = H) gave dihydrobenzofuranol **8a** in 75% yield. Compound **8a** was a mixture of *cis* and *trans* isomers (1.5:1) with regard to ethoxycarbonyl and hydroxyl groups. The stereochemistry of the two isomers was assinged on the basis of ^1H nmr spectra using an anisotropic effect of phenyl group mentioned above. In photoreactions of **2b-c** (R = Me, Et), dihydrobenzofuranols **8b-c** (72-74%) and ethyl acrylates **9b-c** (6-8%) were isolated. The dihydrobenzofuranols **8b-c** were a mixture of *cis* and *trans* isomers (4.1:1 ratio for **8b**, 5.2:1 ratio for **8c**). Ethyl acrylate **9c** was obtained as a mixture of *E* and *Z* isomers, however, it was difficult to isolate each component. The *E* :*Z* ratio was determined from ^1H nmr spectrum of the mixture in which ethoxycarbonyl group deshield hydrogen at the *cis* position. In the case of **2d** (R = *i*-Pr), only dihydrobenzofuranol **8d** (*cis* and *trans* ratio is 5.8:1) was isolated in 75% yield and no ethyl acrylate was obtained. Irradiation of **2e** (R = Ph) gave *cis* isomer exclusively (*cis* and *trans* ratio is 17.8:1).

Reaction pathways of ester compounds **2a-e** are similar to those of ether compounds as shown in Scheme 7. Irradiation of **2a-e** produces 1,5-biradicals **10** via δ-hydrogen abstraction. The biradicals would cyclize directly to dihydrobenzofuranols or cyclize after solvation of hydroxyl group by acetonitrile. Preferential formation of *cis* isomer in each reaction suggests that there is intramolecular interaction like hydrogen bonding between hydroxyl and carbonyl groups in the cyclization step of 1,5-biradicals. This effect would afford cis isomer predominantly. On the other hand, solvated 1,5-biradicals **11** would produce a mixture of *cis* and *trans* isomers because intramolecular hydrogen bonding is impossible and the hydroxyl group becomes larger than free one. In acetonitrile solution, both cyclizations (direct and solvated) would occur at the same time. Solvation of hydroxyl group in 1,5-biradicals is difficult as R becomes bulkier. If ketyl radicals of free 1,5-biradicals **10** and solvated 1,5-biradicals **11** abstract hydrogen from R, ethyl acrylates **9** (6-8%) are produced. Low yields of **9** are attributed to steric effect of phenyl group, because bulky phenyl group make hydrogen abstraction by ketyl radical from R difficult. In the photocyclization of benzophenone esters, rearranged products via 1,3-cyclization were not isolated.

Scheme 7



From the above results photocyclization reactions of benzophenones are useful methods for preparation of dihydrobenzofuranols. The phenyl group of **1** and **2** suppresses 1,3-cyclization reaction of 1,5-biradical intermediates. Photocyclization reactions of benzophenones possessing ethoxycarbonyl group gave *cis* isomers preferentially as a result of intramolecular hydrogen bonding between hydroxyl and carbonyl groups in 1,5-biradicals.

EXPERIMENTAL

The melting points are uncorrected. Column choromatography was performed on silica gel (Wakogel C-200). Unless otherwise stated anhydrous sodium sulfate was employed as the drying agent. Ether refers to diethyl ether. Acetonitrile was dried by distillating over phosphorus pentoxide, then over potassium carbonate. Photoreactions were carried out with 400-W high-pressure mercury lamp (Riko UVL-400 HA) with Pyrex filter. The ir spectra were determined on a Hitachi Model 270-30 IR spectrometer. Unless otherwise stated the ^1H and ^{13}C nmr spectra were determined at 90 MHz and 22.49 MHz on a JEOL-FX 90Q FT NMR spectrometer, using tetramethylsilane as the internal standard.

2-Methoxybenzophenone **1a**.

A mixture of 2-hydroxybenzophenone (2.0 g, 10.1 mmoles), methyl iodide (3.7 g, 26.1 mmoles), tripotassium phosphate (3.3 g, 15.6 mmoles) and acetone (30 ml) was refluxed for 180 minutes. After removal of insoluble materials by filteration the acetone was evaporated. The residue was chromatographed and eluted with benzene to give **1a** (2.7 g, 85%) as a colorless oil, bp 136° at 0.8 Torr [3c, mp 36-38°]; ir (neat): 1660 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 3.71 (s, 3H, OCH_3), 6.88-7.08 (m, 2H, Ar-H_2), 7.24-7.60 (m, 5H, Ar-H_2 and Ph-H_3), 7.68-7.84 (m, 2H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 55.6 (q), 111.6 (d), 120.5 (d), 128.2 (d), 129.0 (s), 129.4 (d), 129.7 (d), 131.9 (d), 132.9 (d), 137.9 (s), 157.4 (s), 196.3 (s).

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 78.98; H, 5.80.

2-Ethoxybenzophenone **1b**.

Compound **1b** (92%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**, bp 150° at 0.8 Torr [3c, mp 38.5-39.0°]; ir (neat): 1650 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 1.06 (t, J = 7 Hz, 3H, OCH_2CH_3), 3.95 (q, J = 7 Hz, 2H, OCH_2CH_3) 6.82-7.08 (m, 2H, Ar-H_2), 7.25-7.60 (m, 5H, Ar-H_2 and Ph-H_3), 7.64-7.84 (m, 2H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 14.2 (q), 64.0 (t), 112.6 (d), 120.5 (d), 128.0 (d), 129.3 (s), 129.5 (d), 129.7 (d), 131.9 (d), 132.5 (d), 138.4 (s), 156.8 (s), 196.6 (s).

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.56; H, 6.25.

2-Propoxybenzophenone **1c**.

Compound **1c** (89%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**, bp 150° at 0.8 Torr [8, bp 204°

at 20 Torr]; ir (neat): 1645 cm^{-1} (Ar-CO); ^{1}H nmr (deuteriochloroform): δ 0.62 (t, J = 7 Hz, 3H, $OCH_2CH_2CH_3$), 1.42 (tq, J = 7 and 7 Hz, 2H, $OCH_2CH_2CH_3$), 3.79 (t, J = 7 Hz, 2H, $OCH_2CH_2CH_3$) 6.80-7.06 (m, 2H, Ar-H_2), 7.20-7.56 (m, 5H, Ar-H_2 and Ph-H_3), 7.66-7.84 (m, 2H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 10.1 (q), 22.2 (t), 69.8 (t), 112.4 (d), 120.4 (d), 128.1 (d), 129.2 (s), 129.4 (d), 129.5 (d), 131.9 (d), 132.5 (d), 138.5 (s), 157.0 (s), 196.7 (s).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.76; H, 6.73.

2-Isobutoxybenzophenone **1d**.

A mixture of 2-hydroxybenzophenone (2.0 g, 10.1 mmoles), isobutyl bromide (4.2 g, 30.7 mmoles), tripotassium phosphate (4.2 g, 19.8 mmoles) and dimethyl sulfoxide (30 ml) was stirred at 60° for 180 minutes. After removal of insoluble materials by filteration the filtrate was poured into water and extracted with ether. The extract was washed, dried and evaporated. The residue was chromatographed and eluted with benzene to give **1d** (2.4 g, 94%) as a colorless oil, bp 157° at 1.5 Torr [8, bp 193° at 14 Torr]; ir (neat): 1660 cm^{-1} (Ar-CO); ^{1}H nmr (deuteriochloroform): δ 0.65 (d, J = 7 Hz, 6H, $OCH_2CH(CH_3)_2$), 1.47-1.94 (m, 1H, $OCH_2CH(CH_3)_2$), 3.63 (d, J = 6 Hz, 2H, $OCH_2CH(CH_3)_2$)), 6.80-7.08 (m, 2H, Ar-H_2), 7.24-7.58 (m, 5H, Ar-H_2 and Ph-H_3), 7.66-7.84 (m, 2H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 18.9 (q), 28.1 (d), 74.7 (t), 112.2 (d), 120.5 (d), 128.1 (d), 129.3 (s), 129.5 (d), 129.7 (d), 132.0 (d), 132.6 (d), 138.6 (s), 157.1 (s), 196.9 (s).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.23; H, 6.95.

2-Benzyloxybenzophenone **1e**.

Compound **1e** (80%) was obtained as colorless crystals from ethanol in a manner similar to the synthesis of **1d**, mp 65-66° [3c, mp 65-67°] ; ir (neat): 1655 cm^{-1} (Ar-CO); ^{1}H nmr (deuteriochloroform): δ 5.00 (s, 2H, OCH_2Ph), 6.80-7.24 (m, 7H, Ar-H_2 and Ph-H_5), 7.26-7.62 (m, 5H, Ar-H_2 and Ph-H_3), 7.68-7.88 (m, 2H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 70.2 (t), 113.0 (d), 121.0 (d), 126.6 (d), 127.5 (s), 127.5 (d), 128.2 (d), 129.6 (d), 129.8 (d), 131.9 (d), 132.6 (d), 136.4 (s), 138.4 (s), 156.4 (s), 196.5 (s).

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.26; H, 5.87.

2-Allyloxybenzophenone **1f**.

Compound **1f** (98%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**, bp 151° at 1.2 Torr; ir (neat): 1670 cm^{-1} (Ar-CO); ^{1}H nmr (deuteriochloroform): δ 4.32-4.52 (m, 2H, $CH_2CH{=}CH_2$), 4.82-5.00 (m, 1H, $CH_2CH{=}CH_2$), 5.00-5.12 (m, 1H, $CH_2CH{=}CH_2$), 5.50-5.94 (m, 2H, $CH_2CH{=}CH_2$), 6.80-7.12 (m, 2H, Ar-H_2), 7.18-7.60 (m, 5H, Ar-H_2 and Ph-H_3), 7.64-7.88 (m, 2H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 69.0 (t), 113.0 (d), 116.7 (t), 120.8 (d), 128.1 (d), 129.5 (s), 129.5 (d), 129.6 (d), 131.9 (d), 132.4 (d), 132.6 (d), 138.2 (s), 156.4 (s), 196.2 (s).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.55; H, 6.09.

2-Benzoylphenoxyacetonitrile **1g**.

Compound **1g** (92%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**, bp 183° at 1.0 Torr; ir (neat): 1670 cm^{-1} (Ar-CO); ^{1}H nmr (deuteriochloroform): δ 4.70 (s, 2H, OCH_2CN), 7.00-7.64 (m, 7H, Ar-H_4 and Ph-H_3), 7.68-7.85 (m, 2H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 54.2 (t), 113.7 (d), 114.8 (s), 123.2 (d), 128.3 (d), 128.5 (d), 129.7 (d), 130.0 (s), 132.0 (d), 133.3 (d), 137.3 (s), 154.1 (s), 195.2 (s).

Anal. Calcd. for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 76.12; H, 4.81; N, 5.74.

2-Isopropoxybenzophenone **1h**.

Compound **1h** (95%) was obtained as a colorless oil in a manner similar to the synthesis of **1a** bp 133° at 0.9 Torr [8, bp 205° at 19 Torr]; ir (neat): 1665 cm^{-1} (Ar-CO); ^{1}H nmr (deuteriochloroform): δ 1.06 (d, J = 6 Hz, 6H, $OCH(CH_3)_2$), 4.43 (septet, 1H, J = 6 Hz, $OCH(CH_3)_2$), 6.80-7.08 (m, 2H, Ar-H_2), 7.20-7.60 (m, 5H, Ar-H_2 and Ph-H_3), 7.62-7.86 (m, 2H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 21.5 (q), 70.6 (d), 113.8 (d), 120.3 (d), 127.9 (d), 129.4 (d), 129.6 (d), 130.0 (s), 131.8 (d), 132.4 (d), 138.4 (s), 155.7 (s), 196.7 (s).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.20; H, 6.99.

Ethyl 2-Benzoylphenoxyacetate **2a**.

Compound **2a** (87%) was obtained as a colorless oil [9] in a manner similar to the synthesis of **1a**; ir (neat): 1760 ($CO_2CH_2CH_3$), 1670 cm^{-1} (Ar-CO); ^{1}H nmr (deuteriochloroform): δ 1.21 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 4.16 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.53 (s, 2H, OCH_2), 6.74-6.90 (m, 1H, Ar-H), 6.94-7.16 (m, 1H, Ar-H), 7.22-7.60 (m, 5H, Ar-H_2 and Ph-H_3), 7.72-7.90 (m, 2H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 14.0 (q), 61.2 (t), 65.8 (t), 112.6 (d), 121.7 (d), 128.1 (d), 129.6 (s), 129.9 (d), 129.9 (d), 131.8 (d), 132.9 (d), 137.7 (s), 155.5 (s), 168.3 (s), 195.9 (s).

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.65; H, 5.77.

Ethyl 2-(2-Benzoylphenoxy)propionate **2b**.

Compound **2b** (83%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**; ir (neat): 1750 ($CO_2CH_2CH_3$), 1660 cm^{-1} (Ar-CO); ^{1}H nmr (deuteriochloroform): δ 1.20 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.24 (d, J = 7 Hz, 3H, $OCHCH_3$), 4.15 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.63 (q, J = 7 Hz, 1H, $OCHCH_3$), 6.66-6.84 (m, 1H, Ar-H), 6.92-7.14 (m, 1H, Ar-H), 7.24-7.60 (m, 5H, Ar-H_2 and Ph-H_3), 7.70-7.90 (m, 2H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 14.1 (q), 17.9 (q), 61.2 (t), 73.4 (d), 111.3 (d), 121.6 (d), 128.0 (d), 129.8 (s), 129.8 (d), 130.0 (d), 131.8 (d), 132.6 (d), 138.2 (s), 155.4 (s), 171.5 (s), 196.2 (s).

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.53; H, 6.19.

Ethyl 2-(2-Benzoylphenoxy)butyrate **2c**.

Compound **2c** (90%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**; ir (neat): 1750 ($CO_2CH_2CH_3$), 1665 cm^{-1} (Ar-CO); ^{1}H nmr (deuteriochloroform): δ 0.61 (t, J = 7 Hz, 3H, CH_2CH_3), 1.21 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.64 (dq, J = 7 and 7 Hz, 2H, CH_2CH_3), 4.16 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.52 (t, J = 6 Hz, 1H, $OCHCH_2CH_3$), 6.64-6.80 (m, 1H, Ar-H), 6.90-7.12 (m, 1H, Ar-H), 7.22-7.56 (m, 5H, Ar-H_2 and Ph-H_3), 7.72-7.92 (m, 2H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 8.7 (q), 14.1 (q), 25.7 (t), 61.0 (t), 77.5 (d), 112.4 (d), 121.3 (d), 128.0 (d), 129.5 (s), 129.7 (d), 129.9 (d), 131.8 (d), 132.6 (d), 138.2 (s), 155.4 (s), 170.7 (s), 196.2 (s).

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.99; H, 6.67.

Ethyl 2-(2-Benzoylphenoxy)-3-methylbutyrate **2d**.

Compound **2d** (82%) was obtained as a colorless oil in a manner similar to the synthesis of **1d**; ir (neat): 1750 ($CO_2CH_2CH_3$), 1665 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 0.52 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 0.73 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.22 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$) 1.80-2.20 (m, 1H, $CH(CH_3)_2$), 4.18 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.37 (d, J = 4 Hz, 1H, $OCHCH(CH_3)_2$), 6.56-6.76 (m, 1H, Ar-H), 6.90-7.12 (m, 1H, Ar-H), 7.24-7.60 (m, 5H, m, 1H, Ar-H_2 and Ph-H_3), 7.72-7.94 (m, 2H, 1H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 14.2 (q), 16.6 (q), 18.5 (q), 31.3 (d), 60.9 (t), 80.9 (d), 111.9 (d), 121.3 (d), 128.1 (d), 129.5 (s), 129.8 (d), 130.0 (d), 131.8 (d), 132.6 (d), 138.2 (s), 155.5 (s), 170.3 (s), 196.4 (s).

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.72; H, 6.86.

Ethyl 2-(2-Benzoylphenoxy)-2-phenylacetate **2e**.

Compound **2e** (52%) was obtained as colorless crystals from ethanol in a manner similar to the synthesis of **1a**, mp 78-79.5°; ir (neat): 1750 ($CO_2CH_2CH_3$), 1660 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform): δ 1.13 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 4.08 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.53 (s, 1H, OCHPh), 6.72-7.24 (m, 7H, Ar-H_4 and Ph-H_3), 7.24-7.62 (m, 5H, Ph-H_5), 7.70-7.96 (m, 2H, Ph-H_2); ^{13}C nmr (deuteriochloroform): δ 13.9 (q), 61.6 (t), 78.8 (d), 112.6 (d), 121.8 (d), 126.5 (d), 128.1 (d), 128.3 (d), 128.6 (d), , 129.6 (s) 129.9 (d), 130.5 (d), 132.1 (d), 132.7 (d), 134.6 (s), 138.2 (s), 154.9 (s), 169.3 (s), 196.4 (s).

Anal. Calcd. for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.80; H, 5.71.

General Procedure for Photocyclization Reactions of Ethers **1a-h** and Esters **2a-e**.

An acetonitrile solution (500 ml) of the starting material (2.00 mmoles) was deoxygenated by bubbling nitrogen gas for 1 hour and then irradiated under monitoring by high performance liquid chromatography (hplc). The irradiation was stopped when the ether almost disappeared. After irradiation the acetonitrile was evaporated under reduced pressure below 40°. The residue was chromatographed and eluted with benzene-ether to give a variety of products.

3-Phenyl-2,3-dihydro-3-benzofuranol **4a**.

Compound **4a** (68%) was obtained as a colorless oil [3c]; ir (neat): 3450 cm^{-1} (OH); ^1H nmr (deuterioacetone): δ 4.44 (d, J = 10 Hz, 1H, 2-H), 4.64 (d, J = 10 Hz, 1H, 2-H), 5.14 (s, 1H, OH), 6.72-7.54 (m, 9H, Ar-H_4 and Ph-H_5); ^{13}C nmr (deuterioacetone): δ 82.4 (s), 86.5 (t), 110.6 (d), 121.4 (d), 125.3 (d), 126.4 (d), 127.5 (d), 128.5 (d), 130.4 (d), 133.7 (s), 145.0 (s), 161.1 (s).

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.46; H, 5.78.

cis-2-Methyl-3-phenyl-2,3-dihydro-3-benzofuranol *cis*-**4b**.

Compound *cis*-**4b** (57%) was obtained as a colorless oil [3c]; ir (neat): 3490 cm^{-1} (OH); ^1H nmr (deuterioacetone): δ 1.39 (d, J = 6 Hz, 3H, CH_3), 4.53 (q, J = 6 Hz, 1H, 2-H), 4.73 (s, 1H, OH) 6.70-7.03 (m, 3H, Ar-H_3), 7.08-7.56 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuterioacetone): δ 12.2 (q), 82.3 (s), 91.0 (d), 110.5 (d), 121.3 (d), 125.6 (d), 126.9 (d), 127.5 (d), 128.4 (d), 130.4 (d), 134.4 (s), 144.4 (s), 160.9 (s).

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.84; H, 6.36.

trans-2-Methyl-3-phenyl-2,3-dihydro-3-benzofuranol *trans*-**4b**.

Compound *trans*-**4b** (24%) was obtained as a colorless oil [4b]; ir (neat): 3450 cm^{-1} (OH); ^1H nmr (deuterioacetone): δ 0.85 (d, J = 7 Hz, 3H, CH_3), 4.78 (q, J = 7 Hz, 1H, 2-H), 5.13 (s, 1H, OH), 6.76-6.99 (m, 3H, Ar-H_3), 7.04-7.40 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuterioacetone): δ 17.2 (q), 85.1 (s), 91.0 (d), 110.7 (d), 121.6 (d), 125.8 (d), 127.5 (d), 127.8 (d), 128.4 (d), 130.4 (d), 134.2 (s), 143.0 (s), 160.7 (s).

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.78; H, 6.34.

cis-2-Ethyl-3-phenyl-2,3-dihydro-3-benzofuranol *cis*-**4c**.

Compound *cis*-**4c** (60%) was obtained as a colorless oil; ir (neat): 3550 and 3500 cm^{-1} (OH); ^1H nmr (deuterioacetone): δ 0.98 (t, J = 7 Hz, 3H, CH_2CH_3), 1.70-2.00 (m, 2H, CH_2CH_3), 4.36 (dd, J = 6 and 8 Hz, 1H, 2-H), 4.73 (s, 1H, OH) 6.70-7.02 (m, 3H, Ar-H_3), 7.09-7.58 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuterioacetone): δ 10.9 (q), 21.2 (t), 82.2 (s), 96.5 (d), 110.5 (d), 121.3 (d), 125.5 (d), 127.0 (d), 127.4 (d), 128.4 (d), 130.4 (d), 134.8 (s), 145.0 (s), 160.7 (s).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.02; H, 6.82.

trans-2-Ethyl-3-phenyl-2,3-dihydro-3-benzofuranol *trans*-**4c**.

Compound *trans*-**4c** (17%) was obtained as a colorless oil; ir (neat): 3450 cm^{-1} (OH); ^1H nmr (deuterioacetone): δ 0.70-1.28 (m, 5H, CH_2CH_3), 4.53 (dd, J = 6 and 8 Hz, 1H, 2-H), 5.14 (s, 1H, OH) 6.77-7.00 (m, 3H, Ar-H_3), 7.00-7.28 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuterioacetone): δ 11.0 (q), 25.6 (t), 84.9 (s), 96.7 (d), 110.9 (d), 121.7 (d), 125.8 (d), 127.7 (d), 127.9 (d), 128.4 (d), 129.1 (d), 130.5 (s), 143.4 (s), 160.9 (s).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.21; H, 6.65.

cis-2-Isopropyl-3-phenyl-2,3-dihydro-3-benzofuranol *cis*-**4d**.

Compound *cis*-**4d** (51%) was obtained as colorless crystals from benzene-hexane, mp 109-109.5°; ir (neat): 3550 and 3520 cm^{-1} (OH); ^1H nmr (deuterioacetone): δ 0.75 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.14 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 2.14-2.64 (m, 1H, $CH(CH_3)_2$), 4.29 (d, J = 10 Hz, 1H, 2-H), 4.79 (s, 1H, OH) 6.64-6.88 (m, 3H, Ar-H_3), 7.00-7.60 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuterioacetone): δ 19.2 (q), 20.4 (q) 28.4 (d), 82.1 (s), 99.3 (d), 110.3 (d), 121.1 (d), 124.5 (d), 126.5 (d), 126.9 (d), 127.8 (d), 130.4 (d), 134.8 (s), 143.9 (s), 159.3 (s).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.47; H, 7.04.

trans-2-Isopropyl-3-phenyl-2,3-dihydro-3-benzofuranol *trans*-**4d**.

Compound *trans*-**4d** (20%) was obtained as a colorless oil; ir (neat): 3460 cm^{-1} (OH); ^1H nmr (deuterioacetone): δ 0.75 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 0.97 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.20-1.76 (m, 1H, $CH(CH_3)_2$), 4.25 (d, J = 10 Hz, 1H, 2-H), 5.23 (s, 1H, OH), 6.70-7.02 (m, 3H, Ar-H_3), 7.02-7.34 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuterioacetone): δ 18.5 (q), 20.0 (q), 29.5 (d), 84.4 (s), 100.0 (d), 110.7 (d), 121.8 (d), 125.1 (d), 127.2 (d), 127.5 (d), 128.2 (d), 130.1 (d), 137.0 (s), 143.5 (s), 160.0 (s).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.42; H, 7.26.

cis-2,3-Diphenyl-2,3-dihydro-3-benzofuranol *cis*-**4e**.

Compound *cis*-**4e** (51%) was obtained as a colorless oil [3c]; ir (neat): 3550 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform, 200 MHz): δ 1.98 (s, 1H, OH), 5.65 (s, 1H, 2-H), 6.92-7.02 (m, 1H, Ar-H), 7.04-7.12 (m, 2H, Ar-H_2), 7.13-7.48 (m, 11H, Ar-H and C_2-Ph-H_5 and C_3-Ph-H_5); ^{13}C nmr (deuterioacetone): δ 83.3 (s), 96.2 (d) 110.9 (d), 121.9 (d), 125.9 (d), 127.4 (d), 127.8 (d), 128.1 (d), 128.2 (d), 128.5 (d), 128.8 (d), 130.6 (d), 134.4 (s), 135.6 (s), 144.3 (s), 160.9 (s).

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.40; H, 5.46.

trans-2,3-Diphenyl-2,3-dihydro-3-benzofuranol *trans*-**4e**.

Compound *trans*-**4e** (30%) was obtained as a colorless oil [3c]; ir (neat): 3450 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform, 200 MHz): δ 3.02 (s, 1H, OH), 5.72 (s, 1H, 2-H), 6.84-7.85 (m, 14H, Ar-H_4, C_2-Ph-H_5 and C_3-Ph-H_5); ^{13}C nmr (deuterioacetone): δ 86.9 (s), 96.6 (d) 110.7 (d), 122.1 (d), 126.0 (d), 126.8 (d), 127.2 (d), 127.6 (d), 127.8 (d), 128.0 (d), 128.9 (d), 130.6 (d), 134.2 (s), 138.1 (s), 142.7 (s), 161.1 (s).

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.44; H, 5.66.

cis-2-Vinyl-3-phenyl-2,3-dihydro-3-benzofuranol *cis*-**4f**.

Compound *cis*-**4f** (39%) was obtained as a colorless oil; ir (neat): 3550 and 3490 cm^{-1} (OH); ^{1}H nmr (deuterioacetone): δ 4.70-4.88 (m, 1H, 2-H), 4.80 (s, 1H, OH), 5.06-5.26 (m, 1H, CH=CH_2), 5.26-5.39 (m, 1H, CH=CH_2), 5.96-6.40 (m, 1H, CH=CH_2), 6.76-7.08 (m, 3H, Ar-H_3), 7.14-7.60 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuterioacetone): δ 83.1 (s), 95.3 (d), 110.6 (d), 119.6 (t), 121.5 (d), 125.5 (d), 126.9 (d), 127.6 (d), 128.4 (d), 130.5 (d), 131.9 (d), 133.8 (s), 144.0 (s), 160.5 (s).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.46; H, 6.04.

trans-2-Vinyl-3-phenyl-2,3-dihydro-3-benzofuranol *trans*-**4f**.

Compound *trans*-**4f** (31%) was obtained as a colorless oil; ir (neat): 3450 cm^{-1} (OH); ^{1}H nmr (deuterioacetone): δ 4.76-5.32 (m, 5H, OH, 2-H and CH=CH_2), 6.78-7.00 (m, 3H, Ar-H_3), 7.04-7.40 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuterioacetone): δ 85.4 (s), 95.5 (d), 110.7 (d), 117.4 (t), 121.7 (d), 125.6 (d), 127.5 (d), 127.6 (d) 128.1 (d),, 130.4 (d), 133.8 (s), 134.8 (d), 142.6 (s), 160.5 (s).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.76; H, 5.87.

cis-2-Cyano-2,3-dihydro-3-benzofuranol *cis*-**4g**.

Compound *cis*-**4g** (32%) was obtained as colorless crystals from benzene-hexane, mp 127-128°; ir (neat): 3430 (OH) and 2260 cm^{-1} (CN); ^{1}H nmr (deuteriochloroform): δ 3.01 (s, 1H, OH), 5.09 (s, 1H, 2-H), 6.84-7.11 (m, 3H, Ar-H_3), 7.11-7.51 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 82.4 (d), 83.7 (s) 111.6 (d), 113.8 (s), 123.4 (d), 125.1 (d), 126.0 (d), 128.8 (d), 128.9 (d), 130.1 (s), 131.6 (d), 140.7 (s), 158.9 (s).

Anal. Calcd. for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 76.02; H, 4.77; N, 5.80.

trans-2-Cyano-2,3-dihydro-3-benzofuranol *trans*-**4g**.

Compound *trans*-**4g** (52%) was obtained as colorless crystals from benzene-hexane, mp 113-114°; ir (neat): 3460 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform): δ 2.88 (s, 1H, OH), 5.28 (s, 1H, 2-H), 6.90-7.12 (m, 3H, Ar-H_3), 7.12-7.52 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 82.5 (d), 86.0 (s) 111.5 (d), 114.6 (s), 123.0 (d), 124.7 (d), 126.8 (d), 128.4 (d), 129.0 (d), 129.7 (s), 131.4 (d), 138.4 (s), 159.2 (s).

Anal. Calcd. for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.83; H, 4.68; N, 5.76.

2, 2-Dimethyl-3-phenyl-2,3-dihydro-3-benzofuranol **4h**.

Compound **4h** (69%) was obtained as colorless crystals from benzene-hexane, mp 55.5-57° [4g]; ir (neat): 3480 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform): δ 0.86 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 2.11 (s, 1H, OH) 6.74-7.02 (m, 2H, Ar-H_2), 7.08-7.56 (m, 7H, Ar-H_2 and Ph-H_5); ^{13}C nmr (deuterioacetone): δ 20.4 (q), 25.8 (q), 85.2 (s), 92.8 (s), 111.1 (d), 120.7 (d), 125.6 (d), 127.2 (d), 127.7 (d), 127.9 (d), 130.4 (d), 132.1 (s), 140.3 (s), 159.2 (s).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.10; H, 6.78.

Ethyl *cis*-3-Hydroxy-3-phenyl-2,3-dihydro-2-benzofurancarboxylate *cis*-**8a**.

Compound *cis*-**8a** (45%) was obtained as colorless crystals from benzene-hexane, mp 131.5-133°; ir (neat): 3420 (OH) and 1745 cm^{-1} ($CO_2CH_2CH_3$); ^{1}H nmr (deuteriochloroform): δ 1.22 (t, J = 7 Hz, 3H, $CO_2CH_2C\mathit{H}_3$), 3.88-4.44 (m, 2H, $CO_2C\mathit{H}_2CH_3$), 5.14 (s, 1H, 2-H), 5.29 (s, 1H, OH), 6.78-7.04 (m, 3H, Ar-H_3), 7.10-7.60 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 14.2 (q), 61.4 (t), 83.7 (s), 91.3 (d), 111.0 (d), 122.1 (d), 125.0 (d), 126.2 (d), 127.7 (d), 128.1 (d), 130.9 (d), 131.1 (s), 142.4 (s), 159.6 (s), 167.5 (s).

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.60; H, 5.46.

Ethyl *trans*-3-Hydroxy-3-phenyl-2,3-dihydro-2-benzofurancarboxylate *trans*-**8a**.

Compound *trans*-**8a** (30%) was obtained as colorless crystals from benzene-hexane, mp 76-77.5°; ir (neat): 3410 (OH) and 1725 cm^{-1} ($CO_2CH_2CH_3$); ^{1}H nmr (deuterioacetone): δ 0.77 (t, J = 7 Hz, 3H, $CO_2CH_2C\mathit{H}_3$), 3.19-3.86 (m, 2H, $CO_2C\mathit{H}_2CH_3$), 5.18 (s, 1H, 2-H), 5.63 (s, 1H, OH), 6.80-7.05 (m, 3H, Ar-H_3), 7.06-7.42 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuterioacetone): δ 13.9 (q), 61.1 (t), 86.3 (s), 93.2 (d), 111.0 (d), 122.2 (d), 125.8 (d), 127.9 (d), 128.1 (d), 128.4 (d), 131.1 (d), 132.7 (s), 142.0 (s), 161.3 (s), 168.4 (s).

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.66; H, 5.52.

Ethyl *cis*-3-Hydroxy-2-methyl-3-phenyl-2,3-dihydro-2-benzofurancarboxylate *cis*-**8b**.

Compound *cis*-**8b** (58%) was obtained as colorless crystals from benzene-hexane, mp 91-92°; ir (neat): 3475 (OH) and 1740 cm^{-1} ($CO_2CH_2CH_3$); ^{1}H nmr (deuteriochloroform): δ 1.12 (s, 3H, CH_3), 1.35 (t, J = 7 Hz, 3H, $CO_2CH_2C\mathit{H}_3$) 2.78 (s, 1H, OH), 4.32 (q, J = 7 Hz, 2H, $CO_2C\mathit{H}_2CH_3$), 6.89-7.16 (m, 3H, Ar-H_3), 7.16-7.58 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 14.1 (q), 22.4 (q), 61.4 (t), 86.5 (s), 94.9 (s), 111.1 (d), 121.5 (d), 125.8 (d), 127.6 (d), 128.0 (d), 128.0 (d), 130.4 (s), 130.8 (d), 139.6 (s), 159.3 (s),170.4 (s).

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.25; H, 6.01.

Ethyl *trans*-3-Hydroxy-2-methyl-3-phenyl-2,3-dihydro-2-benzofurancarboxylate *trans*-**8b**.

Compound *trans*-**8b** (14%) was obtained as colorless crystals from benzene-hexane, mp 123-124.5°; ir (neat): 3450 (OH) and

1720 cm^{-1} ($CO_2CH_2CH_3$); ^{1}H nmr (deuteriochloroform): δ 0.76 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.75 (s, 3H, CH_3), 2.46 (br s, 1H, OH), 3.11-3.81 (m, 2H, $CO_2CH_2CH_3$), 6.79-7.08 (m, 3H, Ar-H_3), 7.09-7.42 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 13.4 (q), 17.6 (q), 61.1 (t), 85.5 (s), 95.7 (s), 110.7 (d), 121.5 (d), 125.3 (d), 126.9 (d), 127.8 (d), 128.0 (d), 130.8 (d), 131.2 (s), 140.4 (s), 160.2 (s),170.9 (s).

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.24; H, 6.08.

Ethyl 2-[2-(α-Hydroxybenzyl)phenoxy]acrylate **9b**.

Compound **9b** (6%) was obtained as a colorless oil ; ir (neat): 3450 (OH) and 1730 ($CO_2CH_2CH_3$) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.27 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 3.22 (br s, 1H, OH), 4.23 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.91 (d, J = 2 Hz, 1H, C=CH_2), 5.65 (d, J = 2 Hz, 1H, C=CH_2), 6.11 (s, , 1H, PhCHOH), 6.79-7.46 (m, 9H, Ar-H_4 and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 14.0 (q), 61.7 (t), 70.8 (d), 105.2 (t), 118.1 (d), 124.5 (d), 126.6 (d), 127.2 (d), 128.1 (d), 128.5 (d), 128.6 (d), 135. 1(s), 142.9 (s), 149.7 (s), 152.7 (s), 162.6 (s).

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.56; H, 6.14.

Ethyl *cis*-3-Hydroxy-2-ethyl-3-phenyl-2,3-dihydro-2-benzofuran-carboxylate *cis*-**8c**.

Compound *cis*-**8c** (62%) was obtained as colorless crystals from benzene-hexane, mp 132-133.5°; ir (neat): 3440 (OH) and 1740 cm^{-1} ($CO_2CH_2CH_3$); ^{1}H nmr (deuteriochloroform): δ 0.87 (t, J = 7 Hz, 3H, CH_2CH_3), 1.24 (q, J = 7 Hz, 2H, CH_2CH_3), 1.35 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$) 2.76 (br s, 1H, OH), 4.34 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 6.82-7.19 (m, 3H, Ar-H_3), 7.20-7.60 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 8.7 (q), 14.2 (q), 29.4 (t), 61.4 (t), 86.4 (s), 98.6 (s), 111.4 (d), 121.4 (d), 125.8 (d), 127.5 (d), 128.0 (d), 128.2 (d), 130.4 (s), 131.0 (d), 139.0 (s), 159.3 (s), 169.6 (s).

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.26; H, 6.54.

Ethyl *trans*-3-Hydroxy-2-ethyl-3-phenyl-2,3-dihydro-2-benzofuran-carboxylate *trans*-**8c**.

Compound *trans*-**8c** (12%) was obtained as colorless crystals from benzene-hexane, mp 111-112°; ir (neat): 3500 (OH) and 1730 cm^{-1} ($CO_2CH_2CH_3$); ^{1}H nmr (deuteriochloroform): δ 0.80 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.05 (t, J = 7 Hz, 3H, CH_2CH_3), 1.95-2.37 (m, 2H, CH_2CH_3) 2.47 (s, 1H, OH), 3.33 (dq, J = 11 and 7 Hz, 1H, $CO_2CH_2CH_3$), 3.71 (dq, J = 11 and 7 Hz, 1H, $CO_2CH_2CH_3$), 6.78-7.08 (m, 3H, Ar-H_3), 7.08-7.40 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 8.8 (q), 13.5 (q), 24.7 (t), 61.1 (t), 85.9 (s), 99.1 (s), 110.9 (d), 121.6 (d), 125.0 (d), 126.7 (d), 127.8 (d), 127.8 (d), 130.8 (d), 131.6 (s), 141.1 (s), 159.6 (s), 170.1 (s).

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.14; H, 6.36.

Ethyl *E*- and *Z*-2-[2-(α-Hydroxybenzyl)phenoxy]crotonoate *E*-**9c** and *Z*-**9c**.

These compounds (8%) were obtained as a mixture (oil) and difficult to isolate each component.

Compound *E*-**8c** had ir (neat): 3470 (OH), 1720 cm^{-1} ($CO_2CH_2CH_3$); ^{1}H nmr (deuteriochloroform): δ 1.17 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.70 (d, J = 7 Hz, 3H, C=$CHCH_3$), 3.76 (br s, 1H, OH), 4.14 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 6.28 (s, 1H, PhCHOH), 6.70 (q, J = 7 Hz, 1H, C=$CHCH_3$), 6.80-7.54 (m, 9H, Ar-H_4 and Ph-H_5).

Compound *Z*-**9c** had ir (neat): 3470 (OH), 1720 cm^{-1} ($CO_2CH_2CH_3$); ^{1}H nmr (deuteriochloroform): δ 1.14 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 2.08 (d, J = 8 Hz, 3H, C=$CHCH_3$), 3.76 (br s, 1H, OH), 4.14 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.97 (q, J = 8 Hz, 1H, C=$CHCH_3$), 6.17 (s, 1H, PhCHOH), 6.80-7.54 (m, 9H, Ar-H_4 and Ph-H_5).

Ethyl *cis*-3-Hydroxy-2-isopropyl-3-phenyl-2,3-dihydro-2-benzofurancarboxylate *cis*-**8d**.

Compound *cis*-**8d** (64%) was obtained as colorless crystals from benzene-hexane, mp 132-133.5°; ir (neat): 3430 (OH) and 1740 cm^{-1} ($CO_2CH_2CH_3$); ^{1}H nmr (deuteriochloroform): δ 0.57 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 0.88 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.39 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.85 (septet, 1H, $CH(CH_3)_2$), 2.85 (s, 1H, OH), 4.37 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 6.84-7.10 (m, 2H, Ar-H_2), 7.15-7.46 (m, 5H, , Ar-H and Ph-H_4), 7.50-7.76 (m, 2H, , Ar-H and Ph-H); ^{13}C nmr (deuteriochloroform): δ 14.2 (q), 16.5 (q), 18.9 (q), 33.2 (d), 61.3 (t), 86.2 (s), 100.6 (s), 110.7 (d), 121.2 (d), 125.4 (d), 127.6 (d), 128.1 (d), 128.5 (d), 130.4 (s), 131.0 (d), 138.8 (s), 160.3 (s),170.4 (s).

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.84; H, 6.94.

Ethyl *trans*-3-Hydroxy-2-isopropyl-3-phenyl-2,3-dihydro-2-benzofurancarboxylate *trans*-**8d**.

Compound *trans*-**8d** (11%) was obtained as colorless crystals from benzene-hexane, mp 121-122°; ir (neat): 3500 (OH) and 1720 cm^{-1} ($CO_2CH_2CH_3$); ^{1}H nmr (deuteriochloroform): δ 0.88 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 0.98 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.10 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 2.72 (septet, 1H, $CH(CH_3)_2$), 2.77 (s, 1H, OH), 3.45 (dq, J = 11 and 7 Hz, 1H, $CO_2CH_2CH_3$), 3.76 (dq, J = 11 and 7 Hz, 1H, $CO_2CH_2CH_3$), 6.76-7.06 (m, 3H, Ar-H_3), 7.08-7.36 (m, 6H, Ar-H and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 13.5 (q), 18.5 (q), 18.9 (q), 33.3 (d), 60.8 (t), 86.3 (s), 100.4 (s), 110.1 (d), 121.7 (d), 123.9 (d), 126.2 (d), 127.4 (d), 127.5 (d), 130.4 (d), 133.0 (s), 143.5 (s), 159.2 (s),170.4 (s).

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.49; H, 6.66.

Ethyl *cis*-3-Hydroxy-2,3-diphenyl-2,3-dihydro-2-benzofurancarboxylate *cis*-**8e**.

Compound *cis*-**8e** (71%) was obtained as a colorless oil; ir (neat): 3460 (OH) and 1740 cm^{-1} ($CO_2CH_2CH_3$); ^{1}H nmr (deuteriochloroform): δ 1.27 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 3.97 (s, 1H, OH), 4.28 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 6.60-7.50 (m, 14H, Ar-H_4, Ph-H_5 and Ph-H_5); ^{13}C nmr (deuteriochloroform): δ 13.9 (q), 62.1 (t), 88.5 (s), 97.3 (s), 110.7 (d), 122.3 (d), 125.3 (d), 126.5 (d), 126.9 (d), 127.2 (d), 127.4 (d), 127.7 (d), 128.0 (d), 130.8 (d), 132.0 (s), 135.2 (s), 139.0 (s), 159.1 (s), 170.0 (s).

Anal. Calcd. for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.78; H, 5.70.

Ethyl *trans*-3-Hydroxy-2,3-diphenyl-2,3-dihydro-2-benzofurancarboxylate *trans*-**8e**.

Compound *trans*-**8e** (4%) was obtained as a colorless oil; ir (neat): 3470 (OH) and 1740 cm^{-1} ($CO_2CH_2CH_3$); ^{1}H nmr (deuteriochloroform): δ 0.85 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 2.14 (s, 1H, OH), 3.32-3.96 (m, 2H, $CO_2CH_2CH_3$), 6.76-7.04 (m, 2H, Ar-H_2), 7.08-7.52 (m, 10H, , Ar-H, Ph-H_4 and Ph-H_5 or

Ph-H_5 and Ph-H_5), 7.64-7.92 (m, 2H, Ar-H_2 or Ar-H and Ph-H); ^{13}C nmr (deuteriochloroform): δ 13.4 (q), 61.7 (t), 87.2 (s), 97.9 (s), 110.7 (d), 122.3 (d), 125.4 (d), 126.9 (d), 127.8 (d), 127.9 (d), 128.0 (d), 128.0 (d), 128.6 (d), 130.8 (d), 132.0 (s), 134.3 (s), 141.5 (s), 158.9 (s), 168.8 (s).

Anal. Calcd. for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.46; H, 5.72.

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